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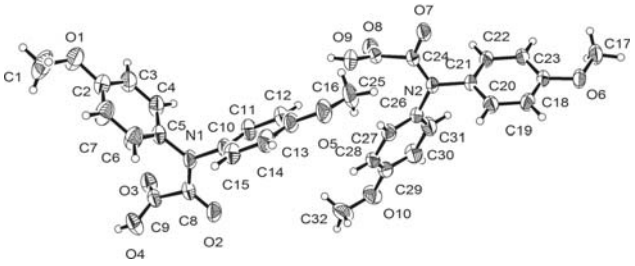
Crystal structure of 2-(*bis*(4-methoxyphenyl) amino)-2-oxoacetic acid, $C_{16}H_{15}NO_5$



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Abstract

$C_{16}H_{15}NO_5$, monoclinic, $P2_1/n$ (no. 14), $a = 6.7689(5)$ Å, $b = 45.219(3)$ Å, $c = 10.1102(6)$ Å, $\beta = 101.360(7)°$, $V = 3033.9(4)$ Å^3, $T = 298(2)$ K.

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Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.30 × 0.22 × 0.17 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Atlas, ω
$2\theta_{max}$, completeness:	58°, 97.3%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15585, 6846, 0.353
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3929
$N(param)_{refined}$:	403
Programs:	CrysAlis^{PRO} [18], SHELX [19], WinGX [20], CHEMDRAW Ultra [21]

Source of material

A solution of oxalyl chloride (1 mole equivalent) in dichloromethane (DCM) was added dropwise to a solution of *bis*(4-methoxyphenyl)amine (1 mole equivalent) in DCM in the presence of triethylamine at room temperature. The mixture was stirred for 1.5 h and water was added. The organic layer was separated, dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give the title compound in 46% yield. The low yield could be a result of half of the amine acting as a base to abstract hydrogen chloride evolved from the reaction. To investigate this issue the reaction was repeated with two equivalents of *bis*(4-methoxyphenyl)amine and no triethylamine. Following aqueous work-up, the crude product was obtained in 75% yield based on oxalyl chloride. Crystallization using acetonitrile gave the title compound as colorless crystals, Mp. 122–123 °C. The NMR spectra recorded at room temperature showed two sets of signals for the two aryl rings, confirming restricted rotation about the C—N bond. The barriers to free rotation in such compounds are already known to be substantial [1–3]. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.04, 6.96 (2 d, $J = 8.5$ Hz, 4 H, H-2/H-6), 6.86, 6.69 (2 d, $J = 8.5$ Hz, 4 H, H-3/H-5), 3.82, 3.71 (2 s, 6 H, OMe); **^{13}C NMR** (100 MHz, DMSO-d_6): δ 164.4 (s, CO_2H), 159.2 (s, C = O), 158.3 (s, C-4), 134.0, 132.8 (2 s, C-1), 129.8, 127.7 (2 d, C-2/C-6), 114.8 (2 d, C-3/C-5), 56.0, 55.8 (2 q, OMe); **ES$^+$—MS**: *m/z* (%) 302 (MH^+, 100), 288 (12), 256 (21), 228 (12); **HRMS** (**ES$^+$**): calculated for $C_{16}H_{16}NO_5$ (MH^+): 302.1028; found: 302.1028. **IR** (FT): ν_{max} 3300, 1740, 1713, 1665, 1500, 1366, 1167 cm^{-1}.

Experimental details

Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined using a ring model. Methyl

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.3411(7)	0.26406(10)	−0.1012(4)	0.1293(17)
H1A	−0.4716	0.2549	−0.1178	0.194*
H1B	−0.3171	0.2728	−0.1831	0.194*
H1C	−0.3359	0.2791	−0.0336	0.194*
C2	−0.2196(4)	0.22459(6)	0.0489(3)	0.0588(7)
C3	−0.0928(4)	0.20057(6)	0.0757(3)	0.0633(7)
H3	0.0066	0.1975	0.0254	0.076*
C4	−0.1137(4)	0.18125(6)	0.1767(3)	0.0610(7)
H4	−0.0282	0.1650	0.1943	0.073*
C5	−0.2587(4)	0.18557(5)	0.2517(2)	0.0477(6)
C6	−0.3827(5)	0.20947(7)	0.2264(3)	0.0724(9)
H6	−0.4807	0.2126	0.2777	0.087*
C7	−0.3637(5)	0.22914(7)	0.1245(3)	0.0789(9)
H7	−0.4489	0.2454	0.1076	0.095*
C8	−0.3962(4)	0.14275(6)	0.3527(2)	0.0507(6)
C9	−0.5151(4)	0.13514(6)	0.2117(3)	0.0504(6)
C10	−0.1313(4)	0.17106(5)	0.4890(2)	0.0496(6)
C11	0.0482(4)	0.15607(6)	0.5151(2)	0.0576(7)
H11	0.0779	0.1424	0.4531	0.069*
C12	0.1853(4)	0.16125(6)	0.6335(3)	0.0629(7)
H12	0.3077	0.1512	0.6510	0.075*
C13	0.1395(4)	0.18131(6)	0.7255(3)	0.0596(7)
C14	−0.0412(5)	0.19644(6)	0.6983(3)	0.0633(7)
H14	−0.0713	0.2101	0.7601	0.076*
C15	−0.1772(4)	0.19128(6)	0.5798(3)	0.0595(7)
H15	−0.2992	0.2014	0.5616	0.071*
C16	0.4445(5)	0.17124(8)	0.8805(3)	0.0927(11)
H16A	0.4118	0.1506	0.8745	0.139*
H16B	0.5101	0.1759	0.9711	0.139*
H16C	0.5328	0.1758	0.8198	0.139*
C17	1.5746(4)	0.04762(7)	1.5043(3)	0.0717(8)
H17A	1.5792	0.0303	1.4501	0.108*
H17B	1.6307	0.0431	1.5969	0.108*
H17C	1.6512	0.0632	1.4738	0.108*
C18	1.2664(4)	0.06381(5)	1.3672(2)	0.0468(6)

C—H bonds were fixed at 0.96 Å and displacement parameters were 1.5 times U_{eq}(C). The methyl groups were allowed to spin about the C—C bond. Aromatic C—H distances were set to 0.93 Å and their U(iso) parameters were set to 1.2 times U_{eq}(C). Hydroxyl O—H distances were set to 0.82 Å and their U(iso) set to 1.5 times U_{eq}(O). Crystal data, data collection and structure refinement details are summarized in Table 1.

Comment

Aryl oxamic acid derivatives have various interesting applications [4–8]. In addition, aryl oxamic acids can be used as intermediates for the synthesis of various classes of compounds including heterocycles [9–12]. Oxamates can be synthesized by the use of various synthetic procedures [13–17].

In the title crystal structure, the asymmetric unit consists of two independent molecules of $C_{16}H_{15}NO_5$. The oxoacetic acid fragments of the molecule are involved in intermolecular hydrogen bonding, of the type O—H···O, with the following geometric parameters: O4···O7 = 2.673(2) Å, O—H···O = 171.0°; and O9···O2 = 2.734(2) Å, O—H···O = 169.9° forming chains along [101].

These hydrogen bonds can be classified as medium strong. Bond lengths and angles in both crystallographically independent molecules are in the expected ranges.

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